Living Radical Polymerization of Methylmethacrylate, Methylacrylate and Their Block Copolymers with Acrylonitrile by Atom Transfer Radical Polymerization

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ABSTRACT

Free radical polymerization with reversible termination has recently generated the longest waiting entry into the field of living and/or controlled polymerization reactions. These methods are known as living radical polymerization and it is found that they proceed in easy conditions and result in narrow polydispersities. Thus, the possibility of living radical polymerization of methylmethacrylate, methylacrylate and their block copolymers with acrylonitrile by atom transfer and with $Cr(OAc)_2$ initiators have been studied. As a consequence, we have synthesized homopolymers with high molecular weights, low polydispersities up to 1.26. Homopolymers and copolymers obtained are characterized with FTIR and GPC.

INTRODUCTION

One of the most useful methods for controlling the molecular weight, polydispersity and the synthesizing of block and well-defined copolymers is by living polymerization method. These techniques also can be used to achieve a high degree of control over polymer chain architecture. Examples of the type of polymers that can be synthesized include block copolymers, comb-shaped polymers, multi-armed polymers, ladder polymers and cyclic polymers. This control of structure, in turn, results in polymers with widely diverse physical properties, even though they are made from readily available low-cost monomers.

A polymerization process is said to be fully living when each polymer unit contains an active site where chain growth occurs indefinitely without termination or chain transfer reactions. Living polymerizations based on anionic, cationic and several types of covalent initiators have been identified, but achieving near ideal properties for a living radical polymerization has proven to be a more elusive objective [1]. Recently, however, living radical polymerization methods are invented to proceed in easier conditions and to result in narrow polydispersities [2, 3].

Two approaches have been followed in efforts to develop living radical polymerization systems. The first approach uses physical methods to prevent

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radicals from contacting each other, thereby preventing their termination [4]. The second approach sometimes called pseudo-living polymerization, involves repeated reinitiation of polymer chains by thermolysis or photolysis of linkages that are built into the chains, [5].

The concept of radical polymerization with reversible termination has been, for many years, relatively successful only in the control of polymer molecular weight, chain ends, and in the preparation of star, block and graft copolymers [6]. Probably, the most influential effort toward living free radical polymerization was generated by using nitroxide-based radicals as reversible terminating agents since they provided the first examples of polymer with narrow molecular weight distribution [7–9].

Organometallic compounds such as cobalt complexes of porphyrine [1], dimethyl glyoxime [10], and some organoaluminium derivatives [11] represent the second class of compounds, which yielded living radical polymerizations via reversible deactivation.

Some of the living polymerization methods, which are being developed, consist of precipitation polymerization [12], template polymerization [13], emulsion polymerization [14], polymerization in inclusion compounds [15], employment of radical complexes [16], inifer techniques [17], plasma induced polymerization [18], polymerization with α-fluoro-acrylamide living radicals [19], and atom transfer radical polymerization, ATRP, [20].

Atom transfer radical addition, ATRA, is a well-known method for carbon-carbon bond formation in organic synthesis. An extension of this technique to ATRP provided a new and efficient way to conduct controlled/living radical polymerizations.

Halogen atom transfer radical polymerization of styrene and methacrylates in bulk have been proceeded with varius types of alkyl halides as initiators and CuX (X=Cl, Br)/2,2′-bipyridine complex as catalyst [20]. The lowest polydispersity was obtained with benzyl chloride/CuCl/2,2′-bipyridine bulk polymerization to be 1.5. Also, an atom transfer radical polymerization of styrene has been proceeding by arenesulphonyl chlorides as initiator and CuCl/2,2′-bipyridine as catalyst [6].

In this work, we have studied the possibility of living radical homopolymerization of methylmethacrylate, methylacrylate with high molecular weights and their block copolymers with acrylonitrile by two living radical polymerization systems, chromium (II) acetate/benzoyl peroxide and atom transfer radical polymerization.

EXPERIMENTAL

Reagents and Solvent
Methylmethacrylate, methylacrylate and acrylonitrile (Merck) were vaccum distilled just before polymerization. Dimethylformamide, DMF, (Merck) was dried by conventional methods.

Initiator
Benzyl chloride was used without purification and benzoyl peroxide (Merck) was recrystallized twice in methanol.

Catalyst
Cuprous chloride was purified and dried by conventional methods before using [21]. Chromium (II) acetate being an unstable compound was prepared in vigorously protected conditions under an argon atmosphere [22].

Ligand
2,2′-Bipyridine (Merck) was used without purification.

EXPERIMENTAL

Homopolymerization and Copolymerization
The general procedure for homopolymerization was as follows:

Chromium (II) Acetate and Benzoyl Peroxide
Before adding the monomer to the polymerization system, 0.085 g (0.5 mmol) chromium (II) acetate and 0.121 g (0.5 mmol) benzoyl peroxide (BPO) were reacted in 10 mL dried DMF at 10 °C for 1 h under argon atomsphere. The solution was cooled to −78 °C

with liquid nitrogen and isoamyl acetate and then 5g (50 mmol) monomer of methylmethacrylate was added under an argon atmosphere, and polymerization was continued at temperature below 30 °C for 48 h. The obtained polymer was dissolved in DMF and it was precipitated in cooled methanol. The yield for the product was 51 %. The second homopolymer, poly-methylacrylate, was prepared under the same conditions mentioned above. The yield obtained was 32 %.

Copolymerization of Methylmethacrylate with Acrylonitrile

In order to carry out the block copolymerization of monomers with chromium (II) acetate and BPO, 0.0121g (0.5 mmol) BPO was allowed to react with 0.085 g (0.5 mmol) chromium (II) acetate in 10 mL DMF at 10 °C for 1 h under argon atomsphere. The solution was cooled to −78 °C and then 5 g (50 mmol) MMA was added, then the polymerization was continued at temperature below 30 °C for 48 h.

After the total MMA was consumed, the remaining monomer was evaporated with vaccum pump, and the temperature of the mixture was cooled to −78 °C and then 2.65 g (50 mmol) acrylonitrile was added and stirred for 48 h at room temperature. The obtained copolymer was precipitated in methanol. Then, the soxhlet apparatus was used for removing unreacted monomers from copolymer product.

Copolymer of methylacrylate with acrylonitrile was prepared at the same conditions that mentioned in the above for copolymer MMA with acrylonitrile.

Atom Transfer Radical Polymerization

To a glass tube, 0.0495 g (0.5 mmol) catalyst (CuCl), 0.234 g (1.5 mmol) ligand (2,2′-bipyridine), 0.0633 g (0.5 mmol) initiator (benzyl chloride) [1:3:1 mol ratio], 5 g (50 mmol) MMA or 5 g (58 mmol) MA and 5 mL dried solvent (DMF) were added. The mixture was degassed 3 times and then it was sealed under vaccum and finally immersed in an oil bath and heated at 130 °C for 1 h. After a certain time, the tube was opened and the mixture was poured in a suitable non-solvent (methanol).

The copolymerization procedure was similar to the above conditions, but halide-ended homopolymer was added to the mixture instead of initiator (benzyl chloride).

Polymer Characterization

Molecular weight and molecular weight distribution were obtained using a Maxima 820 GPC (Instrument: HPLC/GPC Waters and Method: PS-STD -4 Columns).
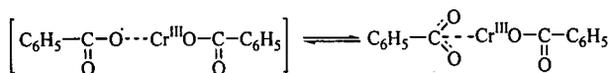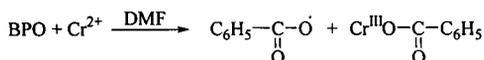
FTIR Spectra were obtained using Shimadzu FTIR-8101M.

RESULTS AND DISCUSSION

Chromium (II) Acetate and BPO System

Before adding the monomer to the polymerization system, Cr^{2+} and BPO with equal moles were reacted in DMF for 1 h. The benzoyloxy radical was formed by the reaction of Cr^{2+} and BPO remained in the ligand field of Cr^{III} and is fixed on the metal center. This free radical is stabilized by resonance with a carbonyl group as shown below (Scheme I).

In order to confirm the existance of living polymer radical, the preparation of block copolymers from homopolymers, the monomer acrylonitrile was added to homopolymers in the presence of Cr^{2+} and BPO initiator system. The separation of homopolymer

$$BPO + Cr^{2+} \xrightarrow{\text{DMF}} C_6H_5-\overset{\overset{\displaystyle \cdot}{|}}{\underset{\underset{\displaystyle O}{||}}{C}}-\dot{O} + Cr^{III}O-\underset{\underset{\displaystyle O}{||}}{C}-C_6H_5$$

$$\left[C_6H_5-\underset{\underset{\displaystyle O}{||}}{C}-\dot{O}\cdots Cr^{III}O-\underset{\underset{\displaystyle O}{||}}{C}-C_6H_5 \right] \rightleftharpoons C_6H_5-C\overset{\overset{\displaystyle O}{.:}}{\underset{\displaystyle O}{.}}--Cr^{III}O-\underset{\underset{\displaystyle O}{||}}{C}-C_6H_5$$

Scheme I

Table 1. FTIR Spectral characterization of polymethylmethacrylate.

Type of bond	Vibration	Region (cm^{-1})
C–H	Stretch	2998
C=O	Stretch	1730
CH$_3$	Bending	1389
C–O	Stretch	1150
CH$_2$	Bending	750

Table 2. FTIR Spectral characterization of copolymer polymethylmethacrylate and polyacrylonitrile.

Type of bond	Vibration	Region (cm^{-1})
C–H	Stretch	2932
C=O	Stretch	1730
CN	Stretch	2241.6
C–O	Stretch	1150
CH$_3$	Bending	1375

MMA or MC from the copolymers was affected by their different degrees of solubility in benzene. Thus, crude polymer product was extracted with benzene in the soxhlet. The unreacted homopolymer MMA or MC was dissolved in benzene and it was separated from block copolymer. Also, all of the initiators were consumed in the preparation of homopolymer MMA or MC, as a result, it was not possible the monomer acrylonitrile being converted to homopolymer of polyacrylonitrile. The homopolymers and copolymers were characterized with FTIR spectroscopy. The results are summarized in Tables 1 and 2.

Also, polymethylacrylate-*block*-polyacrylonitrile copolymer was synthesized in this manner with its FTIR spectrum data as follows: polymethylacrylate: 2998, 1730, 1150, 750 cm^{-1} and polymethylacrylate-*block*-polyacrylonitrile: 2932, 2243, 1730, 866 cm^{-1}.

Transition Metal Catalyzed by ATRP

As described, ATRP can be considered as a consequence of consecutive ATRA. The prerequisite for a successful transformation of transition metal catalyzed ATRP is that the macromolecular halides, R-M$_n$-X, can be effectively activated by transition metal species. The Cu(I) / Cu(II) based redox process in the presence of bipyridine can achieve that goal.

Indeed, to prevent possible polymerization and obtain the monomeric adduct, R-M-X, in good to excellent yields in the ATRA process, organic chemists often use the activated organic halids as radical sources and the alkenes without resonance stabilizing substituents. Under such conditions, the further generation of free radicals/R-M', is kinetically less favorable, since R-M-X is much less reactive than R-X towards the transition metal species.
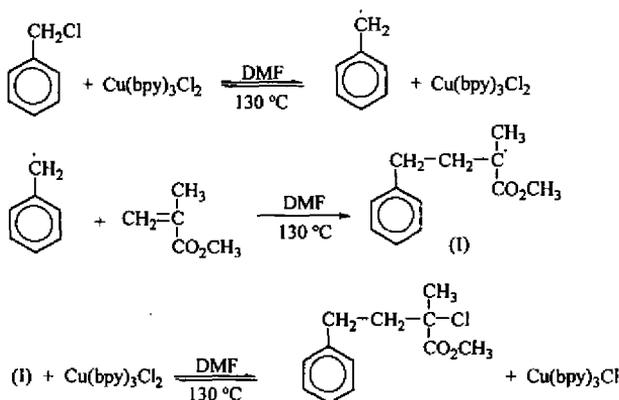
Scheme II

From the results described before, the following parameters are important for promoting the successful transformation of ATRA to ATRP. First, it seems that the use of suitable ligands (e.g., 2,2'-bipyridine), not only increases the solubility of the inorganic salt by coordination to it, but can also facilitate the abstraction of a halogen atom from the initiator, R-X, and from the dormant polymeric halide, R-M_n-X, with the formation of initiating and growing radicals, respectively. Second, the presence of either inductive or resonance stabilizing substituent in the initiator, R-X, is critical for the quantitative generation of initiating radicals, R^.

Finally, the use of a high temperature (about 130 °C) is necessary to complete the polymerization in a reasonable time [20].

All of the ATRPs have been proceeding in the bulk and the mixtures are heterogeneous [20]. The probability of bimolecular termination of growing radicals is increased in the absence of solvent. Some of the vinylic monomers are therefore solid and they cannot be polymerized in bulk in this manner.

Also, a solvent for preparation of block copolymers is necessary as well. Therefore, polymerizations and copolymerizations were accomplished in DMF solvent and the obtained polydispersities were lower than the previous results.

Mechanism

In the ATRP reactions, the catalytic amount of transition metal compound (CuCl) acts as a carrier of halogen atom in a redox process. Initially, the transition metal species, $Cu(bpy)_3Cl$, abstracts the halogen atom, Cl, from the benzyl chloride, to form the oxidized species, $Cu(bpy)_3Cl_2$, and the benzyl radical. In the subsequent step, the benzyl radical reacts with monomer, with the formation of the intermediate radical species. The reaction between radical and
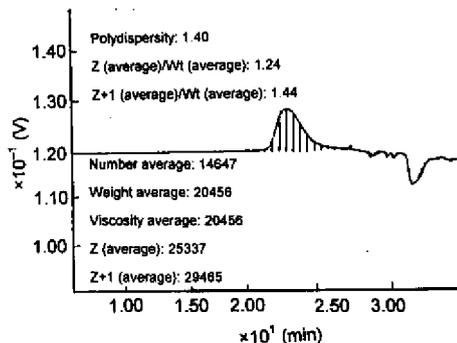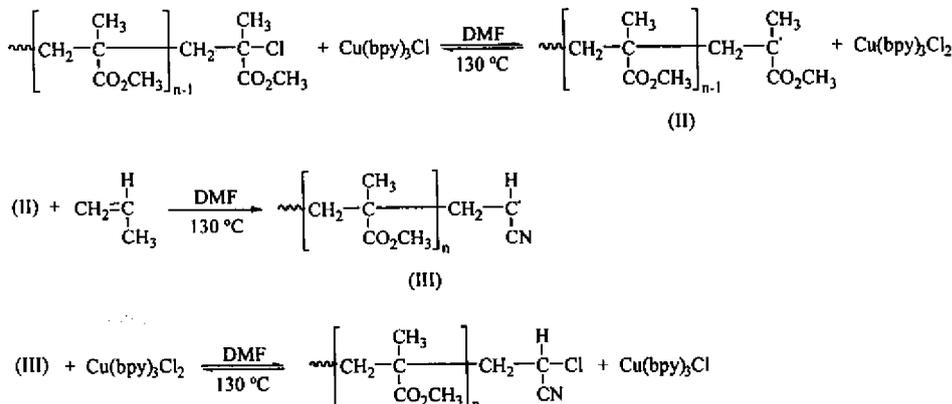

Figure 1. GPC Curve of PMMA obtained from ATRP of MMA in DMF at 130 °C: $[MMA]_0=$ 4.7 M, $[BzCl^a]_0=[CuCl]_0=$ 0.05 M, $[bpy^b]_0=0.15$ M, (BzCl/CuCl/bpy: 1:1:3), Time=2 h, a: benzyl chloride, b: 2,2'-bipyridine.
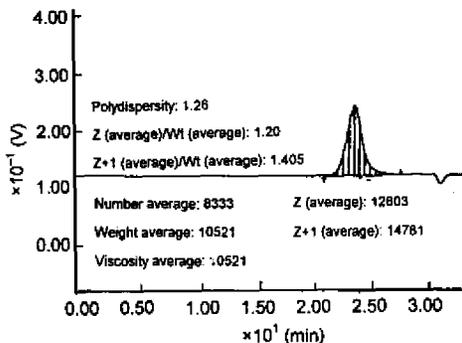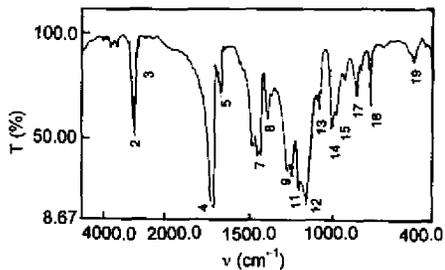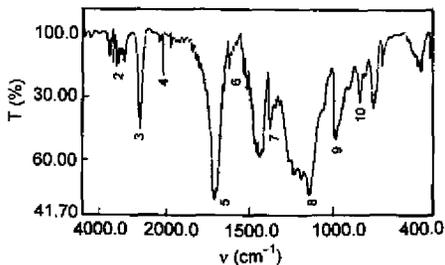

(II)

(III)

Scheme III

Figure 2. GPC Curve of PMA obtained from ATRP of MA in DMF at 130 °C: $[MA]_0=5.8$ M, $[BzCl]_0=[CuCl]_0=0.06$ M, $[bpy]_0=0.18$ M, (BzCl/CuCl/bpy: 1:1:3), Time=2 h.

$Cu(bpy)_3Cl_2$ results in the target product, R-M-X, and regenerates the reduced transition metal species, $Cu(bpy)_3Cl$ (Scheme II).
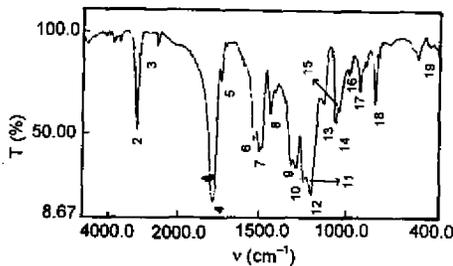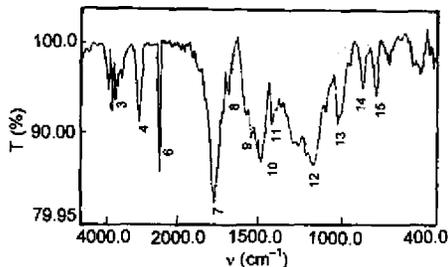

Figure 3. FTIR Spectra of (a) polymethylmethacrylate-*block*-polyacrylonitrile, (b) polymethylmethacrylate-*block*-polyacrylonitrile obtained from the ATRP.

Figure 4. FTIR Spectra of (a) polymethylmethacrylate, (b) polymethylacrylate obtained from the ATRP.

If polymeric halide, $R-M_n-X$, are reactive enough toward $Cu(bpy)_3Cl$, and the monomer is in excess, a number of atom transfer radical additions i.e., such as a living /controlled radical polymerization may occur.

Synthesis of block copolymers was carried out with the use of chlorine-ended polymers instead of benzyl chloride in DMF. Scheme III shows the related mechanism.

Figure 1 shows the GPC chromatogram of poly methylmethacrylate obtained from the living atom transfer radical polymerization method. As shown, polydispersity value is 1.39, while the lowest poly-dispersity obtained using benzyl chloride in bulk polymerization is 1.5 [20].

Figure 2 shows the GPC chromatogram of poly-methylacrylate with polydispersity 1.26. Figure 3a shows the FTIR spectrum of polymethylmethacrylate and Figure 3b shows the spectrum of polymethyl-methacrylate-*block*-polyacrylonitrile copolymer after

purification by benzene with soxhlet. As shown, the new peak in 2241 cm^{-1} is attributed to nitrile group on the second monomer (acrylonitrile). Figure 4a shows the FTIR spectrum of polymethylmethacrylate and Figure 4b shows the spectrum of polymethylmethacrylate.

Recently, a number of polymer chemists were interested in the controlled release of drugs from polymers. Since, the type of drug carrier copolymer (random or block) and second monomer affect the drug releasing process, therefore, the atom transfer radical polymerization provides an effective and useful method for the synthesis of various types of block copolymers containing drugs.

CONCLUSION

Atom transfer radical polymerization reactions have provided a novel method for controlling the polymers syntheses. The primary works have been proceeding in the bulk of monomer and the lowest polydispersity obtained with benzyl chloride initiator was 1.5. In this work, we have polymerized methacrylates and acrylates with the same initiator in DMF and obtained polydispersity as low as 1.26. Therefore, the use of a solvent such as DMF in ATRP decreases the polydispersity and facilitates the synthesis of block copolymers. Also, polymerization with chromium (II) acetate and benzoyl peroxide is a well-defined method for synthesizing polymers with high molecular weights and varius types of block copolymers.

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